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FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (F-POSS)

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ABSTRACT

The wetting of surfaces by water often leads to corrosion and degradation. Data provided by the military services indicate that corrosion is the number one cost driver in lifecycle costs. The total cost incurred by the DoD for corrosion related issues has been estimated to be as high as \$20 billion per year. The wetting of materials by hydrocarbons in automotive and aerospace applications often leads to decreased performance, shorter life-span, and increased cost. Fluorinated polyhedral oligomeric silsesquioxane (F-POSS) compounds have been created and examined to potentially help address these issues. Displaying water contact angles higher than that of PTFE, Fluorodecyl POSS is believed to possess the lowest surface energy of any known solid. The combination of this low surface energy with surface roughness and curvature, similar to that of the Lotus leaf, can lead to the creation of superoleophobic materials. The properties of these materials, as well as their polymer composites, will be discussed.

1. INTRODUCTION

Fluorinated compounds are a logical choice for hydrophobic applications due to their low surface energy. Polyhedral molecules may also improve hydrophobicity by increasing material surface roughness. There have been many reported attempts to synthesize and characterize fluorinated polyhedra. These reports include the fluorination or fluoroalkylation of C₆₀ (1,2). Unfortunately, C₆₀F₄₈ cannot be used as a hydrophobic material, as it is metastable and is hydrolyzed by water (3). The perfluorocarborane species, perfluoro-deca-β-methyl-*para*-carborane, shows remarkable hydrolytic and oxidative stability (4). Fluorinated carbon nanotubes and nanofibers have also been produced (5). These fluorinated polyhedral compounds may be useful in hydrophobic applications, but are generally hazardous to prepare, require air and moisture sensitive manipulations, and have limited economies of scale. For these reasons, alternative fluorinated polyhedral, such as fluorinated polyhedral oligomeric silsesquioxanes (F-POSS) are highly desired (Figure 1).

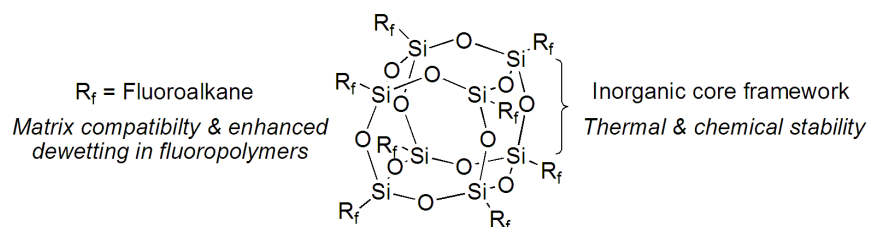


Figure 1. General structure of fluorinated polyhedral oligomeric silsesquioxanes (F-POSS).

POSS are thermally robust cages consisting of a silicon-oxygen core framework possessing alkyl functionality on the periphery. They are used for the development of high performance materials in medical, aerospace, and commercial applications (6,7). POSS molecules can be functionally tuned, are easily synthesized with inherent functionality, and are often commercially available (8). POSS compounds may possess a high degree of compatibility in blended polymers and can easily be covalently linked into a polymer backbone (9). The incorporation of POSS into polymers produces composites with improved properties, such as, glass transition temperature, mechanical strength, thermal and chemical resistance, and ease of processing. Applications include space-survivable coatings (10,11), and ablative and fire-resistant materials (12–14). POSS compounds have a rigid, inorganic core and have been produced with a wide range of organic functionality. POSS can be produced as either completely condensed cages or incompletely condensed cages with silanol groups that allow further modification. Due to their physical size, POSS incorporation in polymers generally serves to reduce chain mobility, often improving both thermal and mechanical properties. Compatibility

The addition of fillers to polymeric matrices is of extreme technological importance. Filler addition can impart enhanced scratch resistance, increase thermal or mechanical properties, and improve processing parameters. There has been much effort to optimize the factors in the addition of filler. Silicate and carbon black based fillers are quite common. They are often inexpensive and their incorporation into many polymer systems is fairly straightforward. When miscibility is a problem, surface modification of the fillers to further enhance their compatibility is widespread. The silylation of surface silanol groups on silica fillers is a good example. Processing is another factor that has been optimized. The use of high shear to break up large agglomerates or aggregates of nanoscopic particles is common. These approaches yield nanoscopic species with large surface areas, which should favor physisorption and/or chemisorption between the polymer chain and the filler.

A number of recent reports have detailed that POSS materials can act as reinforcing fillers (or reinforcing comonomers) in a number of composite systems with nanometer-sized domains (15–17). The results reported herein are somewhat different in that the monodisperse POSS building blocks seem to be rather non-interacting. Specifically, the organic “corona” surrounding the silsesquioxane core is composed of fluoroalkyl moieties. Fluoroalkyl compounds are known to be basically inert. This is largely because they are non-polarizable and have low surface free energies. Fluoroalkyl chains are often rigid, due to steric and electronic repulsion. Similarly, the large corona of the F-POSS compounds should retard the van der Waals attraction between POSS cores. These POSS materials are monodisperse and crystalline. The melting point of the POSS is lower than the processing conditions of the fluoropolymers, so one can safely assume that hard filler effects should not be an issue. In this regard, one may expect that these materials

could exhibit small molecule, solvent like, characteristics. The POSS could be well dispersed and act as a molecular ball bearing. This paper will discuss many of the parameters and physical properties of simple blends of F-POSS materials in fluoropolymer matrices. It will be demonstrated that these simple blends do not rigorously correspond to idealized filled polymer models or to solvent swollen systems. Herein, we describe the properties resulting from the blending of these new POSS compounds into various fluoropolymers.

2. EXPERIMENTAL

2.1 Materials F-POSS compounds **FP**, **FO**, **FD**, and the corner-capped series **2–9** were prepared and fully characterized from previously published procedures (18,19). **6F-BP** PFCB aryl ether polymer (M_n = of 22,000–25,000) was donated and is also commercially available from Tetramer Technologies, L.L.C. and distributed through Oakwood Chemicals, Inc. Polychlorotrifluoroethylene (PCTFE or Neoflon M 400-H) was obtained from Daikin. Hexadecane, and hexafluorobenzene were purchased through Aldrich and used without further purification.

2.3 Single Crystal X-Ray Structural Characterization Crystal data for **FH** and **FD** POSS were collected at $T = 103.0(2)$ K using Bruker 3-circle, SMART APEX CCD with χ -axis fixed at 54.74° , running on SMART V 5.625 program (Bruker AXS: Madison, WI, 2001). Crystallographic data for all structures have been deposited in the Cambridge Crystallographic Data Center (CCDC). Assigned CCDC numbers for **FH** and **FD** are 608207 and 608209, respectively. Copies of the crystallography data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

2.4 F-POSS Coating and Composite Preparation

2.4.1 Spin Cast F-POSS Coating For POSS powders, surfaces were prepared by dissolving the fluoroalkyl POSS in the minimal amount of hexafluorobenzene followed by mechanical agitation. The surfaces were spin cast at 2500 RPM onto borosilicate glass plates producing a well-adhered coating.

2.4.2 F-POSS Solvent Blended Composites with 6F-BP PFCB Aryl Ether Polymer Two methods were used to prepare polymer (or blend) films. For spin cast films, the dried polymer is initially applied in a minimal amount of THF onto a glass substrate and then spin coated at 2500–3000 RPM using a Chemat KW-4A spin coater. The polymer coated substrate is dried in a vacuum oven at 60°C for 24 h. For drop cast films, the polymer dissolved in a minimal amount of THF was dispensed onto a glass plate via a glass pipette and a doctor blade was used to uniformly coat the surface. The polymer solution was allowed to evaporate in a glass enclosure for 48 h and then finally dried in an oven at 60°C for an additional 24 h. Spin and drop cast film thicknesses were approximately 1–2 μm thick and were measured by the Zygo NewView 6300 3D white light optical profiling system.

2.4.3 F-POSS Melt Blended PCTFE Fluoropolymer composites are prepared by adding the designated wt % of **FD** and **FO** POSS melt blended into PCTFE. Melt processing and blending of POSS/fluoropolymers was conducted on a DSM Micro 5 Compounder having a chamber free volume of 5 cm^3 . Powders were pre-mixed in their appropriate ratios and charged to the mixer

imposing a residence time of 5 min under an inert nitrogen atmosphere with the modular heating profile set at a flat 280 °C. Blend extrudates were transferred to a DSM micro-injection molding machine for the fabrication of disks. Samples for dynamic mechanical thermal analysis (DMTA), contact angle measurements, and atomic force microscopy (AFM) were thin films. The films were made by compression molding two grams of the polymer-blend extrudate utilizing a Tetrahedron compression molder. The bars for SEM were also compression molded with the same molding times and temperatures, but utilizing only ½ ton of force.

2.5 Thermo-mechanical Analysis The compression molded films were cut into 3 × 20 mm rectangular samples for dynamic mechanical thermal analysis utilizing a DMTA V from TA Instruments. All fluoropolymer samples were analyzed using a 5 °C temperature ramp and a tensile geometry. The PCTFE samples were each tested from 30 °C to 150 °C. Stress/strain tests were performed on all samples to identify the largest force in which the material exhibited an elastic deformation, thus limiting the pre-tension force used to test the samples. Strain sweeps were also performed to ensure that the testing strain is within the linear viscoelastic region. The F-POSS effect on the thermal stability of the fluoropolymers was examined using a 2050 TGA from Rheometric Scientific in the presence of nitrogen.

2.6 Microscopy The dispersion of the F-POSS was investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2.6.1 Atomic Force Microscopy (AFM) The AFM measurements were performed in tapping mode by a Digital Instruments Dimension 3100 Scanning Probe Microscope (SPM), which utilizes automated atomic force microscopy (AFM) and scanning tunneling microscopy (STM) techniques. Atomic Force Microscopy was conducted on a Nanoscope IV controller (3100 SPM Head) in tapping mode. Etched Silicon probes of nominal spring resonance 300 kHz (spring constant approx. 0.3 mN/m) were used for light tapping (driving amplitude ca 1.1 V) of varying section size at 1-2 Hz collection times (512 points/line). Both the surface topography (height) and phase imaging (indicative of surface mechanical properties) were collected. For melt processed samples, the AFM samples are cut from the compression molded films discussed in the results and discussion section. It was noted that most of the surfaces did not have a significant phase image, which was interpreted as being indicative of relatively uniform surfaces that differed only in surface topography. The surface roughness was dominated by the processing effects, e.g. gross striations indicative of film buckling upon removal. However, fine scale features were resolvable and will be discussed. In the AFM micrograph images, height will be shown on the left side of the figure and a simultaneously collected phase image will be shown on the right.

2.6.2 Scanning Electron Microscopy (SEM) Scanning electron microscopy was performed using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector. Elemental mapping was performed using energy dissipation X-ray analysis with IXRF Systems analysis software. Samples were cut from compression molded bars and the cross-section was imaged. Furthermore, an elemental mapping of the surface is discussed.

2.7 Static and Dynamic Contact Angle Contact angle analysis was performed on a Contact Angle analyses were performed on a FDS Dataphysics Contact Analyzer System using a syringe metering pump. Deionized water (18 MΩ·cm, Barnstead) was used as the interrogating

liquid. Small drops of water (approximately 2-5 μL) were accurately metered onto a flat surface, and the full screen image of the drop was captured with the frame grabbing software coupled to a CCD camera operating at the optimized zoom and contrast. The contact angles were determined via the software suite or *via* graphical fitting of the contact tangents in the captured image. Both approaches gave the same nominal value within ± 2 degrees. Static water contact angle values reported were an average of three values measured on various areas of the surface.

3. RESULTS AND DISCUSSION

3.1 F-POSS Synthesis F-POSS compounds fluorodecyl (**FD**), fluoroctyl (**FO**), and fluorohexyl (**FH**) were produced by the base-catalyzed hydrolysis of trialkoxy silanes (Figure 2). These compounds tend to condense into T_8 cages, rather than cage mixtures, as has been previously observed in the base-catalyzed synthesis. The yields for these reactions are often nearly quantitative. This is significant because the usual method to produce T_8 cages is the acid-catalyzed hydrolysis of trichlorosilanes, which produces an undesirable acidic by-product.

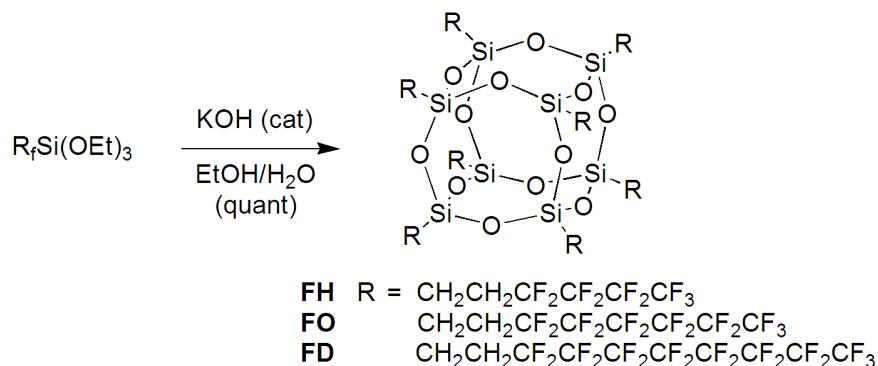


Figure 2. Synthesis of octahedral F-POSS compounds.

Hepta(3,3,3-trifluoropropyl)tricycloheptasiloxane trisodium silanolate **1** was used as an intermediate for the preparation F-POSS compounds **2–7** by “corner-capping” with fluoroalkyltrichlorosilanes (Figure 3). The intermediate salt (**1**) is stable in air, but decomposes to silsesquioxane resin upon exposure to moisture. The intermediate adduct is the result of a pathway to fully condensed cage structures by simply controlling feedstock stoichiometry.

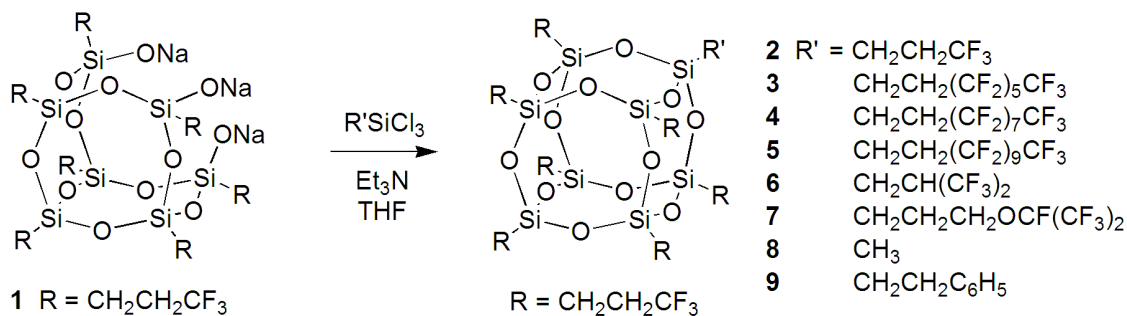


Figure 3. Synthesis of corner-capped F-POSS compounds.

Corner-capping with commercially available functionalized fluoroalkyltrichlorosilanes afforded diverse architectures with linear fluoroalkyl chains (**2–5**), a branched hexafluoroisopropyl (**6**), and a heptafluoroisopropoxypropyl ether (**7**). F-POSS **2** (synonymously denoted **FP**) possesses octahedral symmetry like those F-POSS series **FH**, **FO**, and **FD**. This corner-capping methodology was employed in the incorporation of methyl (**8**) and phenylethyl (**9**) hydrocarbon groups in the predominantly fluorinated environment.

3.2 F-POSS Properties Selected properties of F-POSS compounds are illustrated in Table 1. These F-POSS compounds are only soluble in fluorinated solvents such as AK-225G (Asahi Glass) and hexafluorobenzene. Unlike most non-fluorinated POSS compounds, thermogravimetric analysis (TGA) indicates F-POSS volatilize rather than decompose. No residue remains after heating under either nitrogen or dry air. **FD** POSS is the most stable compound, subliming at over 300 °C. F-POSS are also very dense, high molecular weight materials. For example, **FD** POSS has a molecular weight of 3993.54 g/mol and a density of 2.067 g/cm³.

The structure–property relationship of F-POSS compounds was studied from experimental melting points (T_m) obtained from the amorphous powders precipitated from methanol. As a general trend, melting points become depressed as fluoroalkyl chain lengths increase due to weaker intermolecular van der Waal attractions. All F-POSS compounds were observed to possess narrow melting points as high molecular weight compounds indicative of high purity (Table 1). In all cases, no decomposition was observed for these compounds at the melting point. It is clear from the data in Table 1 melting point properties are primarily dominated by substrate structure and not solely on wt % F content. In this case, the low melting points of extended F-POSS compounds **3–5** would be valued for low temperature melt processing with polymers affording blended composites.

The F-POSS compounds were spin cast from hexafluorobenzene onto a glass substrate. The spin casting produces well-adhered, white powder-like films and did not visually expose any of the glass substrate. Their static (or advancing) contact angles were measured using deionized water and hexadecane as test fluids. Hexadecane is a standard test fluid for determining the oil repellency (or oleophobicity) of a material. The F-POSS series measured water contact angles are on average 50° higher than for hexadecane contact angles. As a consequence of the highest wt % F content, **FD** produced the highest water and hexadecane static contact angle of 154°, and 87°, respectively. Since its water contact angle was greater than 150°, the surface of **FD** as a spin cast powder is classified as being formally ultrahydrophobic.

For the F-POSS octamer series of **FP**, **FH**, **FO**, and **FD**, there is a near linear progression of water and hexadecane contact angle in relation to the increasing fluorine content of the F-POSS compounds. This is clearly shown by a 13% increase in water contact angle from **FP** (38.2% fluorine content) to the **FH** (57.2% fluorine content) compound. It would appear a leveling-off effect is anticipated past the series fluoroalkyl substitution beyond the **FO**, since a negligible increase of 5% was observed from **FH** (57.2% fluorine content) to **FO** (61.9% fluorine content). However, the **FD** (64.7% fluorine content) has an abrupt increase of 12% from **FO** POSS. A similar trend was observed for hexadecane contact angles, but the standard deviation would indicate oleophobicities of **FH**, **FO**, and **FD** are the same.

Table 1. Selected Properties of F-POSS Compounds

Cmpd	Fluoroalkyl Group	$\theta_{\text{water}}/^{\circ}$	$\theta_{\text{hex}}/^{\circ}$	$T_{\text{m}}/^{\circ}\text{C}^a$	wt % F ^b
FP (2)	R = R' = CH ₂ CH ₂ CF ₃	116	69	234–237	38.5
FH	R = CH ₂ CH ₂ (CF ₂) ₃ CF ₃	131	80	121–123	57.2
FO	R = CH ₂ CH ₂ (CF ₂) ₅ CF ₃	138	82	120 ^c	61.9
FD	R = CH ₂ CH ₂ (CF ₂) ₇ CF ₃	154	87	150 ^c	64.7
3	R = CH ₂ CH ₂ CF ₃ R' = CH ₂ CH ₂ (CF ₂) ₅ CF ₃	109	77	104–106	45.0
4	R = CH ₂ CH ₂ CF ₃ R' = CH ₂ CH ₂ (CF ₂) ₇ CF ₃	112	76	88–90	50.5
5	R = CH ₂ CH ₂ CF ₃ R' = CH ₂ CH ₂ (CF ₂) ₉ CF ₃	112	80	105–107	51.8
6	R = CH ₂ CH ₂ CF ₃ R' = CHCH(CF ₃) ₂	122	74	234–236	40.9
7	R = CH ₂ CH ₂ CF ₃ R' = CH ₂ CH ₂ CH ₂ OCF(CF ₃) ₂	108	73	70–71	40.4
8	R = CH ₂ CH ₂ CF ₃ R' = CH ₃	102	51	168–170	35.9
9	R = CH ₂ CH ₂ CF ₃ R' = CH ₂ CH ₂ C ₆ H ₅	106	45	109–111	33.0

^a Melting point capillary. ^b Calculated from molecular formula. ^c DSC analysis at midpoint.

Generation of potential energy surfaces for a packed lattice of **FH** and **FD** provided a better understanding of the observed increase in water contact angle of **FD** POSS. As shown in Figure 4, **FH** POSS is compared with **FD** POSS which showed a molecular roughening arranged in a corrugated fashion. **FP** and **FO** POSS also showed similar flat packing planes compared with **FH** POSS. This increased molecular-scale, calculated to nanometer-scale, surface roughness presumably contributes to the dramatic increase in the water contact angle of **FD** to 154°, which is approximately 23° higher than **FH**.

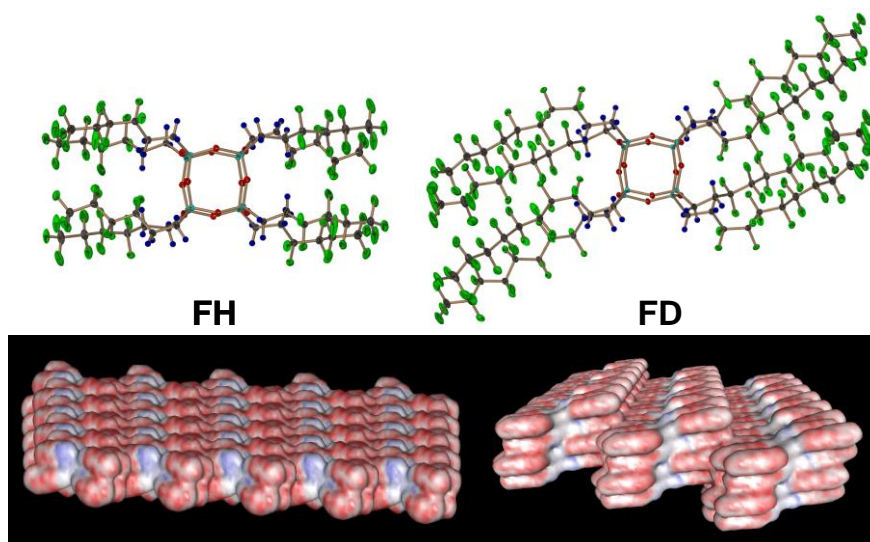


Figure 4. X-ray crystal structures (top) of **FH** and **FD** POSS and their accompanying electrostatic potential diagrams.

The potential energy surfaces shown in Figure 4 represent crystalline surfaces obtained by single crystal X-ray analysis. It should be noted the water contact angles for the observed trend were analyzed from spin cast, semicrystalline powder films. AFM analysis revealed the spin cast **FD** POSS surface produced a root-mean-square (RMS) roughness of approximately 4 μm (Figure 5).

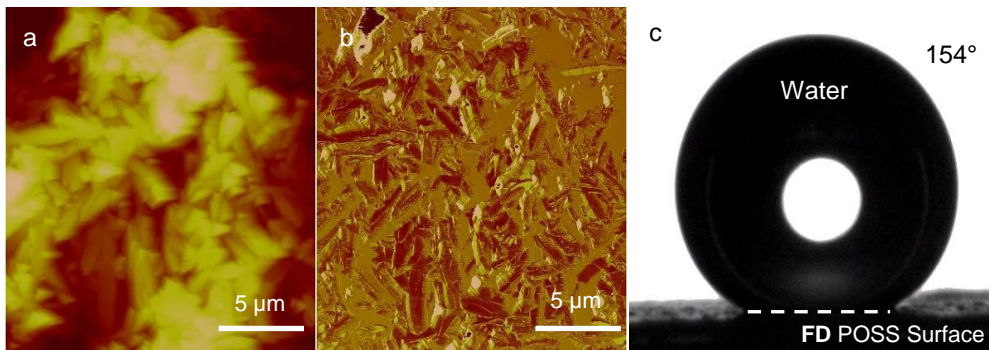


Figure 5. AFM height (a) and phase (b) image of spin cast film (SCF) of **FD** POSS showing micrometer-size crystalline aggregates and water drop on SCF of **FD** POSS with a measured contact angle of 150° (c).

3.2 POSS Fluoropolymers Selected F-POSS compounds possessing the highest hydro- and oleophobicity were blended into several fluoropolymers in order to develop a preliminary study of F-POSS compatibility in polymer matrices. For the purposes of this paper, **FD** POSS **6F-BP** perfluorocyclobutyl (PFCB) aryl ether (Figure 6) polymer blends will be used to describe F-POSS dispersion and its affect on surface wettability (section 3.2.1). **FO** and **FD** POSS blends in commercial PCTFE will be used to describe melt processing (section 3.2.2), thermo-mechanical (section 3.2.3), and surface properties (section 3.2.4).

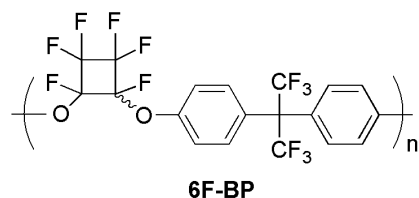


Figure 6. 6F-Biphenyl (**6F-BP**) perfluorocyclobutyl (PFCB) aryl ether polymer.

3.2.1 Dispersion The level of dispersion of F-POSS compounds into polymer systems is largely dependent on surface chemistry. PFCB aryl ether polymers are of interest in a multitude of materials applications, specifically their ability to produce optically transparent, processable films (20). Increasing **FD** POSS wt % loadings blended with **6F-BP** PFCB aryl ether polymer showed a gradual increase in water, but profound increase in hexadecane contact angle (Figure 7). The **6F-BP** PFCB aryl ether polymer is intrinsically hydrophobic and produced water and hexadecane contact angles of 95° and 27°, respectively. **FD** POSS loadings up to 15 wt % developed a plateau from static water contact angle; the blend showed an overall 32% increase in water contact angle (124°) at this loading compared with unblended **6F-BP**. At optimized **FD** POSS loadings of 10 wt %, a maximum hexadecane contact angle of 80° was observed, increasing hexadecane repellency by 158%. While films prepared from 15 wt % **FD** POSS loading still appeared transparent and homogenous, 20 wt % **FD** POSS produced slight phase separation. At 30 wt % **FD** POSS, significant incompatibility was observed producing brittle, opaque films with crystalline aggregates on the film surface.

It is noted that when blended surfaces were tilted beyond 90° or even inverted (180°), water remained pinned to the film; this is not the case with powdered surfaces solely prepared from spin cast fluorinated POSS. A surface with a contact angle of 90° or higher is considered a “non-wetting” surface, while a surface with a contact angle below 90° is considered “wetting.” Addition of F-POSS produces a “non-wetting” surface.

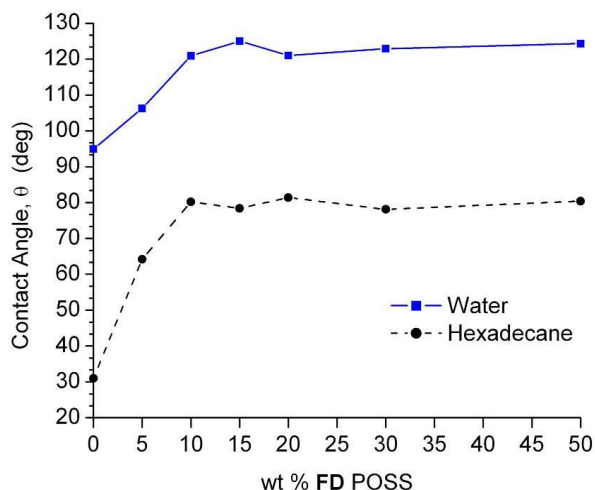


Figure 7. Water and hexadecane contact angles of various wt % of **FD** POSS blended into **6F-BP** PFCB aryl ether polymer.

Dynamic water and hexadecane contact angles were evaluated to determine the degree of hysteresis of **FD POSS** blended into **6F-BP PFCB** aryl ether polymer. The angles of advancing (θ_a) and receding (θ_r) of water and hexadecane were obtained by placing a liquid drop on the surface and tilting the stage of the goniometer. The results of the measurements for water and hexadecane are shown in Figure 8 and Figure 9, respectively. At all wt % of **FD POSS** blended into the polymer, the water and hexadecane drops remained pinned on the surface, even when the stage was tilted 90° . Initially, the advancing and receding angles were taken at the onset of liquid drop perturbation on the uphill and downhill side during as the stage was tilted. However, these measurements were difficult to assess “by eye” and produced a high deviation in recorded values. Therefore, the dynamic angles were recorded at a 90° tilt in order to ensure consistency. These results indicate a condition of high surface hysteresis where the surface energy (γ_{sv}) exceeds the surface tension (γ_{sl}) of the liquid drop.

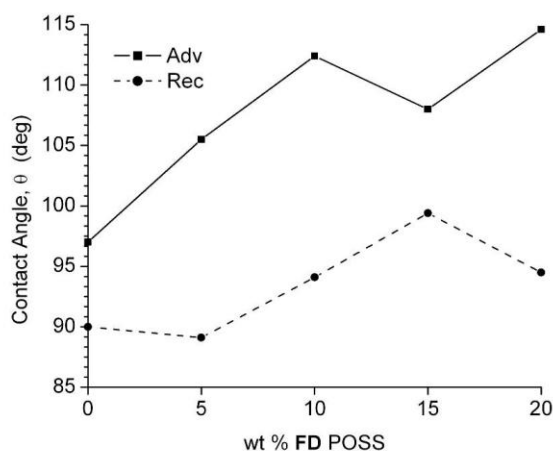


Figure 8. Dynamic water contact angles of various wt % of **FD POSS** blended into **6F-BP PFCB** aryl ether polymer.

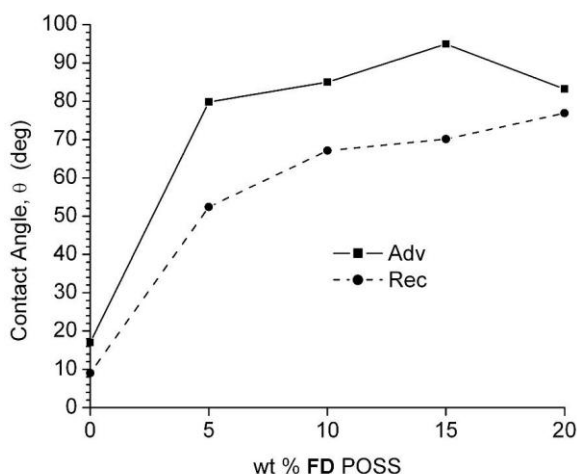


Figure 9. Dynamic hexadecane contact angles of various wt % of **FD POSS** blended into **6F-BP PFCB** aryl ether polymer.

Blending **FD** POSS into the **BP-6F** PFCB aryl ether polymer introduced additional fluorine content and increased surface roughness. As demonstrated in the beginning of this chapter, the relationship of contact angle and surface energy is governed by Young's equation which relates interfacial tensions among the surface to the liquid and gas phases of water (21). Furthermore surface roughness imparts increased hydrophobicity to material as demonstrated by Cassie and Wenzel (22,23).

Atomic force microscopy (AFM) analysis of 15 wt % **FD** blend compared with the virgin **6F-BP** PFCB aryl ether polymer showed a marked increase in surface roughness (Figure 10). From AFM analysis, unblended **6F-BP** polymer and 15 wt % **FD** POSS composite blend gave a measured surface roughness (RMS) of 0.527 nm and 1.478 nm, respectively. The incorporation of the fluorinated **FD** POSS structures produced this three-fold increase in surface roughness possibly due to blooming and aggregation of these structures on the surface during the spin casting process. The increase in surface roughness was nearly 1 nm (the difference of 1.278 nm and 0.527) due to the inclusion of **FD** POSS. Such a slight increase in surface roughness is usually not enough to influence the overall macroscopic properties such as the contact angle. It is generally accepted average surface roughness (R_a) < 100 nm has little affect on contact angles and hysteresis. Therefore, it is presumed the low surface energy fluorine content contributed by fluorinated POSS has the most influence on the surface contact angle, whereas the surface roughness is an important, but minor contributing parameter. On-going surface characterization is being investigated in order to determine the concentration gradient of the fluorinated POSS structures on the surface compared to those entrained in the bulk material.

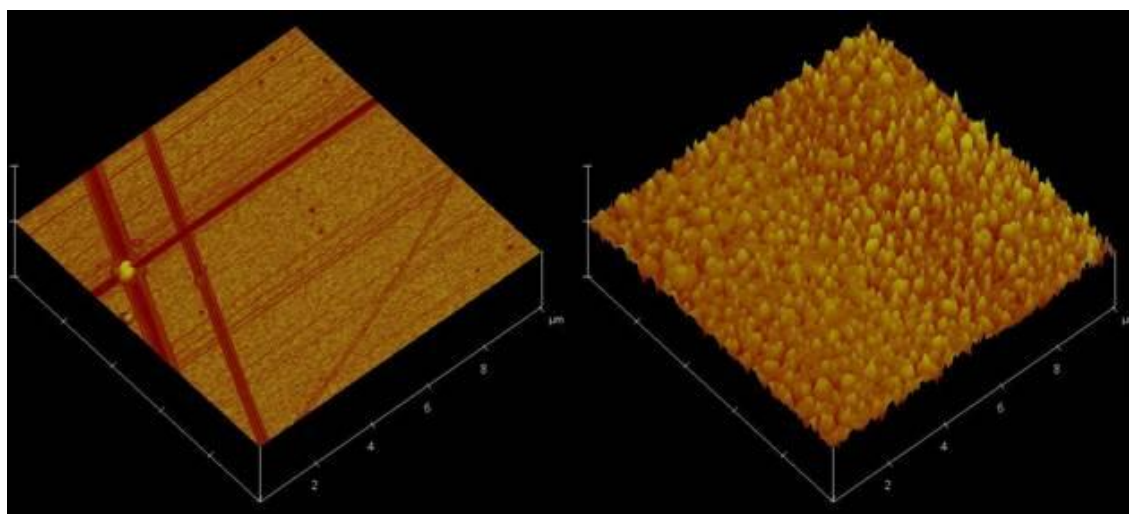


Figure 10. AFM image of **6F-BP** PFCB aryl ether polymer (left) and of 15 wt % **FD** POSS blend.

3.2.2 Melt Processability The processability of the samples was compared using torque and load of the compounder motor, a measure of the pressure generated in the mixer. The pressure is generated in the mixer due to the conical design of the mixer. For a constant volume of material compounded and a fixed screw speed, the pressure generated is proportional to the viscosity of the material. The lower the pressure, the lower the viscosity, and the easier the material is to process. The second measure of processability is the torque output by the motor. This gives an

indication of the mechanical energy put into the system and is proportional to the current used by the motor. Hong et al. utilized a similar measure to characterize the processability of polyethylene and hyperbranched polymer blends (24). The lower the torque output the more processable the polymer (for a given screw speed).

These two measures of the processability of the polymer blends were recorded at 30 s. intervals during processing. It was found, within a 95% confidence interval, the load and torque values were constant for the duration of processing excluding the first 30 s. Therefore, an average value for both torque and load is assigned to each processing run. In order to investigate the effect of the addition of F-POSS, relative torque and relative load values were computed utilizing the average values in comparison to the average values found for the unfilled resins.

Figure 11 show the relative torque and load values with respect to the wt % of POSS added for the PCTFE blends. The solid symbols represent the relative torque values where the relative load results are illustrated by the open symbols. The square symbols symbolize the results of the **FD** POSS blends and the circular symbols show the **FO** POSS blend results. One will note that PCTFE processability is improved by greater than 30 wt %.

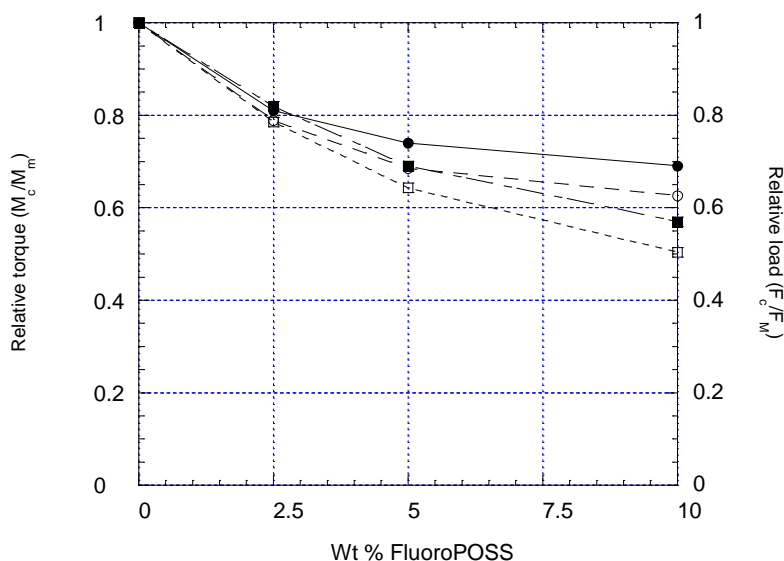


Figure 11. Effect of **FD** POSS on processing variables torque and load for PCTFE blends.

3.2.3 Thermo-mechanical Analysis In order to determine the effect of the F-POSS on the mechanical properties of PCTFE, dynamic mechanical analysis (DMTA) was performed. Figure 12 illustrates the storage moduli for the PCTFE blends. One will notice only a small decrease in the modulus values between the filled and unfilled samples.

Figure 13 shows the loss moduli for the PCTFE blends. One will notice that, similar to the storage modulus curves in Figure 12, the loss moduli of the PCTFE blends are very similar to the unfilled PCTFE curve with only a slight decrease. The mechanical properties of the fluoropolymer are only slightly altered by the addition of F-POSS. The possible exception to this is the composite with 10 wt % **FD** POSS. This sample was very difficult to mold into quality films for testing. The poor quality of the films tested may lead to the scatter seen in the

data and possibly the lower temperature for the peak in the loss modulus curve. For this study, the glass transition temperature of the polymer is defined as the peak in the loss modulus curves. The addition of F-POSS to PCTFE decreases the glass transition temperature approximately two degrees. The variation in glass transition temperature seen with the addition of F-POSS is small enough to be statistically insignificant.

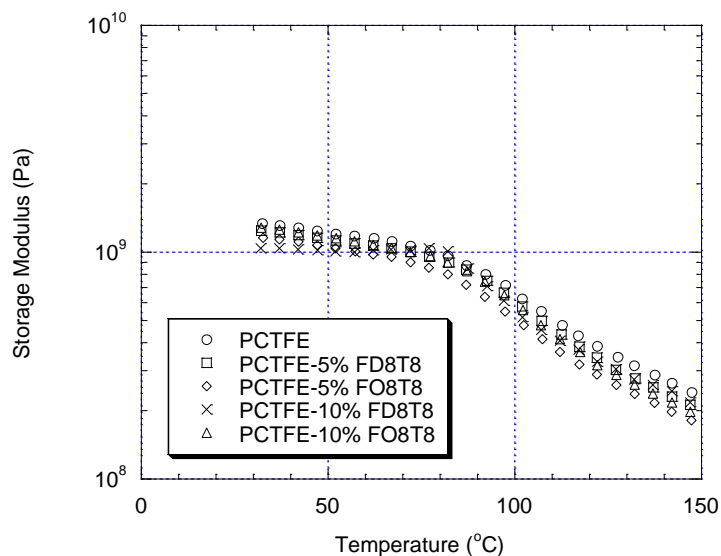


Figure 12. Storage modulus data for **FD** POSS/PCTFE films.

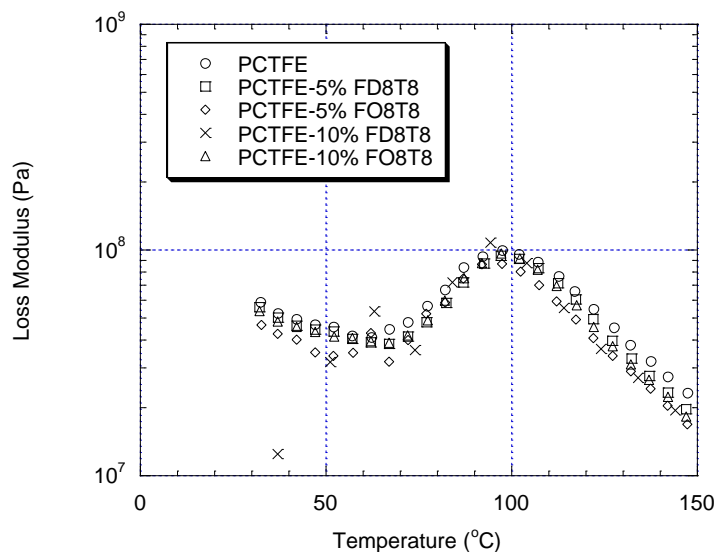


Figure 13. Loss modulus data for **FD** POSS/PCTFE films.

3.2.4 Surface Properties While fluoropolymers are known for their hydrophobicity and low coefficients of friction, incorporation of F-POSS may help to improve these properties even further. Contact angles have been obtained on PCTFE nanocomposites containing **FO** and **FD** POSS.

Technologies that may benefit from the blending of F-POSS into fluoropolymers include abrasion resistance, lubricity, anti-icing, and non-wetting applications. Figure 14 (left image) shows a drop of water on the surface of a PCTFE film; the contact angle was measured at 88°. A drop of water on the surface of a PCTFE blend containing 10 wt % **FD** POSS (Figure 14, right image) produced a contact angle measured at 128°. There is a 40° increase in contact angle with a modest 10 wt % added **FD** POSS.

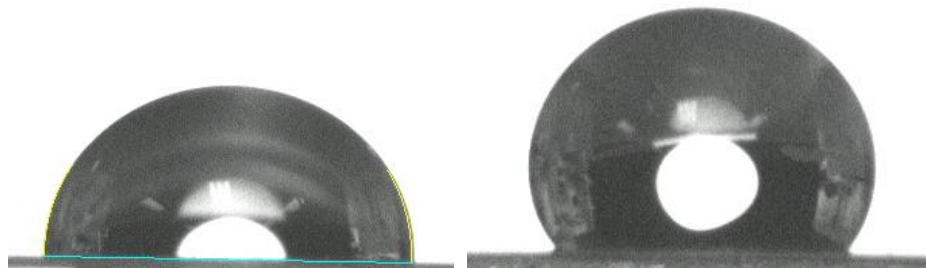


Figure 14. Water contact angle of 88° on PCTFE film (left) and 128° on PCTFE film containing 10 wt % **FD** POSS (right).

Similar to PFCB aryl ether polymer solvent blended coatings with **FD** POSS, application of hexadecane on the PCTFE melt blended compositions with **FD** POSS resulted in improvement of oleophobicity with hexadecane contact angles increasing from approximately 32° to 58°.

4. CONCLUSIONS

Various fluorinated polyhedral oligomeric silsesquioxanes (F-POSS) have been solvent or melt blended into a variety of fluoropolymers. These fluoropolymers include perfluorocyclobutyl (PFCB) aryl ether polymers and poly(chlorotrifluoroethylene) (PCTFE). The composite blends produce well-dispersed F-POSS based on microscopy analysis. The fluoroalkyl groups on the F-POSS cages demonstrate good miscibility in selected fluoropolymer matrices. These F-POSS fluoropolymer composites may be useful as low friction surfaces either as bulk components or coatings. Contact angle measurements of the POSS fluoropolymers show an improvement of water and hexadecane contact angles over the unfilled materials. The low surface energy POSS compounds also appear to act as a processing aid during fluoropolymer processing, significantly reducing both the torque and load measurements in the extruder. Thermal and mechanical properties of the blended fluoropolymers do not compromise the integrity of the unfilled polymers. Work continues to encompass the other F-POSS as simple drop-in modifiers for other fluoropolymers.

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